

10/665310 F  
02-14-05



(11) Publication number: **0 559 418 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **93301541.4**

(51) Int. Cl.<sup>5</sup>: **E21B 43/26**

(22) Date of filing: **01.03.93**

(30) Priority: **02.03.92 US 844167**

(43) Date of publication of application:  
**08.09.93 Bulletin 93/36**

(84) Designated Contracting States:  
**DE FR GB NL**

(71) Applicant: **TEXAS UNITED CHEMICAL  
CORPORATION  
2000 West Loop South Suite 990  
Houston, TX 77027 (US)**

(72) Inventor: **Mondshine, Thomas, C.  
6619 Burning Tree Street  
Houston, Texas 77036 (US)**

(74) Representative: **Fisher, Adrian John et al  
CARPMAELS & RANSFORD 43 Bloomsbury  
Square  
London WC1A 2RA (GB)**

(54) **Process for decomposing polysaccharides in alkaline aqueous systems.**

(57) Alkaline earth metal or transition metal peroxides are used as a delayed breaker in alkaline aqueous fluids containing a water soluble hydrophilic polysaccharide polymer hydrated therein. The peroxide is activated by increasing the temperature of the fluid. The invention is particularly useful for the delayed break of hydraulic fracturing fluids containing hydroxypropyl guar polymer.

**EP 0 559 418 A2**

Jouve, 18, rue Saint-Denis, 75001 PARIS

BACKGROUND OF THE INVENTION

The present invention relates to the decomposition of hydrophilic polysaccharide polymers in aqueous systems, and, more particularly, to a method of breaking down such polymers when they are present in the filter cake deposited from a well working fluid, and to a method of breaking a fracturing fluid containing such polymers.

PRIOR ART

Fluids of various types are used in well working operations. One major use of fluids is in earth formation fracturing. In fracturing the formation, a fluid is introduced into the well at a rate and pressure sufficient to produce one or more fractures in the formation and/or enlarge or extend existing fractures. The fluid normally contains a propping agent which is deposited in the fractures to keep the fractures from closing. In water base fluids, it is usually necessary to employ an additive which imparts sufficient viscosity to the fluid to maintain entrained solids in suspension. Representative additives include hydrophilic polysaccharide polymers such as guar gum, hydroxypropyl guar, carboxymethyl hydroxypropyl guar, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, and the like, all as is well known in the art. The hydrophilic polymer may be crosslinked as is also well known in the art. See for example Mondshine U.S. Patent No. 4,619,776.

Once the formation is fractured and the proppant placed, it is desirable to reduce the viscosity of the fluid so that it may be easily removed from the formation. This is known as "breaking" the fluid. Conventionally, this breaking of the aqueous gel or fluid is carried out by adding a viscosity reducing agent, commonly called a "breaker," to the formation at the desired time. Unfortunately, the techniques and materials used often result in insufficient breaking (viscosity reduction) or premature, early breaking of the fluid. Premature breaking of the fluid causes a reduction in the viscosity of the fracturing fluid prior to the desired termination of the fracturing operation, thereby reducing the overall effectiveness of the operation. See for example Wyant et al. U.S. Patent No. 3,163,219 and Nolte U.S. Patent No. 4,506,734.

In recent years, it has been discovered that the permeability of proppant packs placed by the fracturing fluid may be significantly damaged by the gelling agents commonly used in hydraulic fracturing fluids. Studies have shown that the permeability is significantly impaired by the polymer residue even though sufficient breaker concentrations have been added to effectively reduce the fluid viscosity. See for example the following references, incorporated herein by reference: (1) SPE Technical Paper 20135, "Breaker Concentrations Required To Improve The Permeability Of Proppant Packs Damaged By Concentrated Linear And Borate-Crosslinked Fracturing Fluids," H.D. Brannon and R.J. Pulsinelli, March 8-9, 1990; (2) SPE Technical Paper 19402, "Evaluation Of The Breaker Concentrations Required To Improve The Permeability Of Proppant Packs Damaged By Hydraulic Fracturing Fluids," H.D. Brannon and R.J. Pulsinelli, February 22-23, 1990; (3) SPE Technical Paper 19433, "Encapsulated Breaker For Aqueous Polymeric Fluids," J. Gulbis, M.T. King, G.W. Hawkins, and H.D. Brannon, February 22-23, 1990; (4) SPE Technical Paper 21716, "Increased Breaker Concentration In Fracturing Fluids Results In Improved Gas Well Performance," J. Elbel, J. Gulbis, M. T. King, and J. Maniere, April 7-9, 1991.

The proppant pack permeability damage caused by the concentration of polymers in the pack has been observed to be significantly reduced only by the addition of elevated concentrations of the breaker. Unfortunately, the viscosity reduction of the fracturing fluid is accelerated by increasing breaker concentration and fluid temperature. Thus it has been proposed to control and/or delay the activity of the breaker by coating the breaker. See for example the following U.S. Patents: Burnham et al. -4,202,795; Nolte -4,506,734; Wales et al. -4,741,401.

Fluids containing hydrophilic polysaccharide polymers are also used in various other well working or drilling operations. See for example Mondshine U.S. Patents No. 4,175,042; 4,186,803; 4,369,843; 4,620,596; 4,621,692; and Dobson, Jr. et al. U.S. Patent No. 4,822,500. In such fluids typically a "filter cake" is deposited on the sides of the borehole or over packed perforation channels. This filter cake will contain the hydrophilic polymer. It is desirable to remove the filter cake before placing the well on production in order to allow the well fluids to flow unrestricted to the wellbore.

It is therefore highly desirable to decompose the hydrophilic polysaccharide polymer(s) present in hydraulic fracturing fluids or in the filter cake deposited within a well during various well working operations after such polymer(s) have accomplished their intended function.

Calcium peroxide is disclosed for use in bleaching compositions at a pH from 9.6 to 12.13 in Moyer U.S. Patent 3,251,780, and at a pH from 3.0 to 9.5 in Moyer U.S. Patent No. 3,259,584. Calcium peroxide particles coated with a coating agent containing a water-insoluble compound having a melting point of at least 50°C are disclosed in Gago U.S. Patent No. 4,293,426.

Alter U.S. Patent No. 3,167,510 discloses a process of breaking well treating fluids containing guar gum using alkali metal persulfate oxidizers, and discloses at column 2, lines 56-62 and column 3, lines 1-5, that calcium peroxide,  $\text{CaO}_2$ , does not function as a breaker in his process.

## 5 SUMMARY OF THE INVENTION

In accordance with the present invention, processes are provided for: breaking fracturing fluids containing hydrophilic polysaccharide polymers; decomposing hydrophilic polysaccharide polymers contained within proppant-packs; and decomposing hydrophilic polysaccharide polymers contained within filter cakes present  
10 in a well.

These processes are accomplished by oxidizing the hydrophilic polysaccharide polymers with an alkaline earth or transition metal peroxide as disclosed hereinafter.

I have now found that alkaline earth-metal peroxides and zinc peroxide can be used to decompose water soluble hydrophilic polysaccharide polymers, hereinafter sometimes referred to as HPP, present in aqueous  
15 systems such as fracturing fluids, proppant-packs, and filter cakes in a well.

A high concentration of a peroxide selected from the group consisting of alkaline earth metal peroxides, zinc peroxide, and mixtures thereof, hereinafter sometimes referred to collectively as AEMP, can be added to fracturing fluids at ambient temperature without causing a significant viscosity decrease of the fluid until desired, i.e., until placement of the proppant in the fracturing fluid within the fractures created in the well by the fluid. The breakdown rate of the HPP will depend on the temperature of the fluid, the concentration of the  
20 AEMP, the particular AEMP present in the fluid, and the pH of the fluid. The fluid must have an alkaline pH otherwise the AEMP is solubilized at a rate which causes premature breaking of the fluid. Desirably the pH of the fluid is greater than about 7, preferably greater than about 9, and most preferably greater than about 10. The breakdown rate of the HPP increases as the temperature of the fluid increases. Thus for any given  
25 fluid temperature and pH, the breakdown rate of the HPP can be controlled by the proper selection of the AEMP and its concentration.

While the invention is susceptible of various modifications and alternative forms, specific embodiments thereof will hereinafter be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the invention  
30 is to cover all modifications and alternatives falling within the spirit and scope of the invention as expressed in the appended claims.

The compositions can comprise, consist essentially of, or consist of the stated materials. The method can comprise, consist essentially of, or consist of the stated steps with the stated materials.

## 35 DESCRIPTION OF THE INVENTION

I have found that AEMP in alkaline aqueous fluids containing HPP such as fracturing fluids will thermally decompose and release polymer breaking hydrogen peroxide. For any given fluid the rate and quantity of hydrogen peroxide released is controlled by the temperature of the fluid and the type and quantity of AEMP present  
40 in the fluid.

The AEMP are stable and only slightly soluble at ambient temperatures but thermally decompose and release hydrogen peroxide when subjected to heat. This enables the AEMP to provide a delayed breakdown of the fluid, i.e., sufficient AEMP can be incorporated into a fluid containing a HPP without excessive breakdown of the HPP until the fluid has accomplished its desired function.

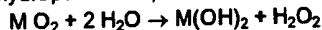
45 Alkaline earth peroxides are known water insoluble compounds. See for example the following references, incorporated herein by reference: (a) "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals," Ii'ya Ivanovich Vol'nov (Translated by J. Woroncow, Edited by A.W. Petrocelli), Plenum Press, New York, 1966; (b) "Kirk-Othmer Encyclopedia of Chemical Technology," Third Edition, Vol. 17, John Wiley & Sons, 1982, pp. 1-26.

50 Inorganic peroxide compounds are commonly described as compounds whose structures include the peroxo-group,  $\text{—O—O—}$ . Simple peroxide compounds include peroxides in which the peroxo-group is bonded to a metallic atom via ionic bonding, and includes hydroperoxides characterized by the presence of the hydroperoxyl ion  $(\text{HO}_2)^-$ . Complex peroxide compounds include peroxides in which the peroxo-group as such, or in the form of  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$ , is bonded to the metallic atom by a covalent bond. Complex peroxide compounds also include the addition compounds formed with crystallized hydrogen peroxide.

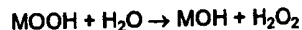
55 The characteristic properties of peroxide compounds both simple and complex, are: the formation of hydrogen peroxide upon reaction with dilute acid solution, the liberation of oxygen as a result of thermal decomposition, and the liberation of oxygen upon reaction with water and other chemical agents. Further character-

ization is possible by dividing the simple inorganic peroxide compounds into four groups: (1) hydroperoxide, characterized by the  $(\text{HO}_2)^-$  ion; (2) peroxides, characterized by the  $(\text{O}_2)^{2-}$  ion; (3) superoxides characterized by the  $(\text{O}_2)^-$  ion; and (4) ozonides, characterized by the  $(\text{O}_3)^-$  ion.

The hydrolysis of peroxides and hydroperoxides proceeds as follows:



and



where M = metal. For this reason, peroxides and hydroperoxides are considered as being derived from hydrogen peroxide by replacement of one or both the hydrogen atoms by metal atoms.

Complex peroxide compounds include peroxyhydrates, for example,  $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ , and peroxyhydrate hydrates, for example,  $\text{BaO}_2 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ .

Peroxides of calcium, strontium and barium belong to the  $\text{M}^{2+}\text{O}_2^{2-}$  type of peroxide compound, while peroxides of magnesium and zinc, of general formula  $\text{MO}_2 \cdot x\text{H}_2\text{O}$ , probably belong to the HO-M-OOH type where the covalent bond between the hydroperoxyl group and the metal atom is the same as that in hydrogen peroxide.

Calcium peroxide is generally prepared by industrial processes which provide a product containing 60-75 wt. %  $\text{CaO}_2$ . Reaction of  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$  with solutions containing greater than 20 wt. % of hydrogen peroxide results in the formation of calcium peroxyhydrate,  $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ . Strontium peroxide, industrial grade, generally contains 80-95%  $\text{SrO}_2$ . Industrial grade barium peroxide generally contains up to about 90%  $\text{BaO}_2$ . Depending on its method of production, industrial grade magnesium peroxide contains from about 25%  $\text{MgO}_2$  to about 50%  $\text{MgO}_2$  and generally is a mixture of peroxide, oxide, and magnesium oxide hydrate. Industrial grade zinc peroxide contains about 55%  $\text{ZnO}_2$ .

The water soluble hydrophilic polysaccharide polymers useful in this invention may be any of such polymers well known in the art. See for example the book "Handbook of Water-Soluble Gums and Resins," Robert L. Davidson, Editor, McGraw-Hill Book Co., 1980, incorporated herein by reference. Representative polymers include water soluble salts of alginic acid, carrageenan, gum agar, gum arabic, gum ghatti, gum karaya, gum tragacanth, locust bean gum, tamarind gum, cellulose derivatives such as hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, hydroxyethyl carboxymethyl cellulose, and the alkyl cellulose ethers, starch derivatives such as carboxymethyl starch, hydroxyethyl starch, hydroxypropyl starch, and crosslinked starch ethers, guar gum and its derivatives, such as hydroxypropyl guar, hydroxyethyl guar and carboxymethyl guar, and biopolymers such as xanthan gum, gellan gum, welan gum, and the like.

The polymers useful in fracturing fluids are glycans containing monosaccharide units having adjacent cis-hydroxyl groups attached to the sugar ring structure, or derivatives thereof. Such groups, unlike hydroxyl groups adjacent to one another in the trans position, are highly susceptible to oxidation and undergo extensive complex forming and cross-linking reactions with a variety of polyvalent cation and boron-containing cross-linking agents. These reactions permit the ready formation of polysaccharide gels of the type utilized in accordance with the invention. Monosaccharide units having adjacent cis-hydroxyl groups include D-mannose, D-mannuronic acid and D-mannopyranose. Glycans containing such units may be homoglycans or heteroglycans. Typical homoglycans include 1,4'-D-mannose linear polysaccharides such as ivory nut mannan, wood mannan and salep mannan; 1,4'-D-mannuronic acid linear polysaccharides such as alginic acid; 1,2',1,3'- and 1,6'-D-mannose branched chain polysaccharides such as yeast mannan; 1,4'-D-mannose branched chain polysaccharides such as the mannan of *Porphyra umbilicis*; and other D-mannose polysaccharides such as mannocarlose. Heteroglycans containing adjacent cis-hydroxyl groups include 1,4'- and 1,6'-D-galactose and D-mannose polysaccharides such as guaran and locust bean gum; glucomannans such as those obtained from *Amorphophallus* and *Aloe vera*; galactomannans such as those obtained from the endosperms of the honey locust, flame tree, Kentucky coffee bean, paloverde, tarn, lucerne, huizache and *Sophora japonica*; D-arabinose and D-mannose polysaccharides; D-glucose, D-mannose and D-galactose polysaccharides; and D-galactose, D-mannose and N-acetyl-D-glucosamine polysaccharides. It will be understood that all of the above named materials are not equally effective for purposes as viscosifiers for fracturing fluids and that certain materials will be preferred over others.

Preferred polysaccharides for use in fracturing fluids include the galactomannans derived from vegetable sources. Upon hydrolysis those materials yield the two simple sugars, mannose and galactose. Analyses have indicated them to be long chain polymers of D-mannopyranose units linked at the  $\beta$ -1,4-positions and having D-galactopyranose units located as chains on the molecule. The D-galactopyranose units are connected to the C<sub>6</sub> atoms of the D-mannose units which make up the main structural framework. The ratio of D-galactose to D-mannose in the galactomannans varies from about 1:1.2 to about 1:2, depending upon the particular vegetable source from which it is obtained. In all cases, however, the mannose residues have cis hydroxyl groups at the C<sub>6</sub> and C<sub>3</sub> positions, accounting for the gelling properties of the galactomannans and making them useful

for purposes of the present invention.

Galactomannans are major constituents of the seeds of a variety of plants. Plants from which they be extracted include tara, *Caesalpinia spinosa*; huizache, *Caesalpinia cacalaco*; locust bean, *Ceratonia seliqua*; palo-verde, *Cercidium torreyanum*; the flame tree, *Delonix regia*; guar, *Cyanopsis tetragonolobus*; the honey locust, *Gleditsia triacanthos*; the Kentucky coffee bean, *Gymnocladus dioica*; the prairie mimosa, *Desmanthus illinoensis*; senna, *Cassia leprocarpa*; rattlebox, *Crotalaria intermedia*; clover, *Trifolium pratense*; and soy bean hulls, *Glycine soja*. In recent years guar seeds cultivated in the southwestern section of the United States have provided much of the galactomannan marketed commercially. Because the guar seed product is available from a number of commercial sources at relatively low cost, galactomannan derived from this source is particularly preferred for purposes of the invention.

The hydroxypropyl ether derivative of guar gum is the preferred polymer used in the fracturing fluid industry at the present time.

The preferred polymers useful in well workover and completion fluids are derivatives of cellulose, derivatives of starch, and various biopolymers. Representative cellulose derivatives include hydroxyethyl cellulose, carboxymethyl cellulose, hydroxyethyl carboxymethyl cellulose, hydroxypropyl cellulose, and the like. Representative starch derivatives are hydroxyethyl starch, hydroxypropyl starch, carboxymethyl starch, and such starch derivatives further crosslinked with a difunctional molecule, such as epichlorohydrin or phosphorous oxychloride. The preferred starch derivative is epichlorohydrin crosslinked hydroxypropyl starch as disclosed in Dobson, Jr. et al. U.S. Patent No. 4,822,500, incorporated herein by reference. Representative biopolymers are xanthomonous (xanthan) gum, gellan gum (see Baird et al. U.S. Patent No. 4,503,084), and welan gum (see Kang et al. U.S. Patent No. 4,342,866).

The concentration of the AEMP must be sufficient to provide the desired degree of breakdown of the polymer in the treated fluid at the temperature to which the fluid is heated and aged. Generally a concentration in the range from about 0.01 kg/m<sup>3</sup> to about 1.8 kg/m<sup>3</sup> will be incorporated into the fracturing fluid or other aqueous fluid containing the HPP. Preferably the concentration of calcium peroxide is in the range from about 0.01 kg/m<sup>3</sup> to about 1.0 kg/m<sup>3</sup> and the concentration of magnesium peroxide is in the range from about 0.18 kg/m<sup>3</sup> to about 1.8 kg/m<sup>3</sup>.

The process of the invention is accomplished by adding the AEMP to an alkaline aqueous fluid having a HPP hydrated therein, and increasing the temperature of the fluid to activate the peroxide and decompose or breakdown the HPP. The fluid should be aged at the desired temperature for a period of time sufficient to effect the desired degree of breakdown of the polymer, which as discussed hereinbefore, is dependent upon the particular AEMP added and its concentration. In the case of a fracturing fluid, the temperature is increased by leaving the fluid within a subterranean formation after creating fractures therein.

As is well known in the art, certain HPP may be crosslinked. Crosslinking increases the effective molecular weight of the polymer creating an enhanced viscosity increase and even gelation of the aqueous fluid containing the hydrated HPP. See for example Mondshine U.S. Patent No. 4,619,776, incorporated herein by reference. The AEMP is effective as a delayed breaker for decomposing the HPP in both its crosslinked and non-crosslinked forms, provided that the hydrated HPP is present in an aqueous fluid at an alkaline pH, most preferably at a pH of at least about 10.

It is speculated that some breakdown of the HPP takes place as soon as the AEMP is added to the fluid containing the HPP. However, with the proper selection of the particular AEMP and its concentration, based on the temperature to which the fluid will be heated as discussed herein, the breakdown rate of the HPP will be insufficient to prevent the fluid from accomplishing its intended purpose. Yet, once the fluid has accomplished its intended purpose, the HPP will breakdown. In the case of a fracturing fluid, the fluid can then be flowed back out of the fractures leaving behind the proppant packed within the fractures.

The AEMP is an essentially insoluble particulate material at ambient temperature. As long as it remains insoluble, it will be concentrated in leak off derived filter cakes at the formation-fracture interface. Upon aging at the temperature of the formation, the AEMP will become activated and, hence, react with and decompose the HPP. This will increase the conductivity of the proppant-pack within the fractures.

The solubility rate and hence the reactivity rate of the AEMP can be decreased if necessary by coating the AEMP. The coating material may be a water-insoluble, oil-soluble material, or a water-soluble material that is only slowly soluble in the aqueous fluid containing the hydrated HPP. See for example Wyant U.S. Patent No. 3,163,219, incorporated herein by reference. Alternatively, the AEMP can be incorporated into an enclosure member as disclosed in Walles et al. U.S. Patent No. 4,741,401, incorporated herein by reference, or in hollow or porous, crushable beads, as disclosed by Nolte U.S. Patent No. 4,506,734, incorporated herein by reference.

Where desired, the reactivity of the AEMP can be enhanced by the addition of a catalyst to the fluid containing the HPP before or after the addition of the AEMP to the fluid. Suitable catalysts include the transition metal cations, such as copper, nickel, cobalt, iron, manganese, and the like which have been complexed to

insure their stability in alkaline solutions. Known complexing agents include such chelating agents as ethylenediamine-tetraacetic acid, nitrilotri (methylenephosphonic acid), and the like. The catalyst may be coated to delay its reaction with the AEMP until after the fluid containing the HPP has performed its intended function.

Where desirable, the AEMP can be used in conjunction with known breakers for aqueous fluids containing HPP. Such commonly used breakers include oxidizing agents and enzymes. Specific examples of breakers include sodium persulfate, ammonium persulfate, potassium persulfate, alpha and beta amylases, amyloglucosidase, aligloglucosidase, invertase, maltase, cellulase, hemicellulase, and the like. These breakers may also be coated or otherwise treated as disclosed herein to delay their effect on the HPP.

The following examples describe the manner and process of making and using the invention and set forth the best mode contemplated by the inventor for carrying out the invention, but are not to be construed as limiting the invention.

The fracturing fluid used to evaluate the AEMP breakers of this invention was prepared as follows: hydroxypropyl guar was dispersed and hydrated in tap water at a concentration of 4.8 kg/m<sup>3</sup>; 0.3% by volume of a 35% by weight potassium carbonate solution was added while mixing at a speed sufficient to create a vortex in the fluid; the desired concentration of AEMP was then added and dispersed in the fluid; 0.25% by volume of FRACSAL WW crosslinking agent was then added and mixed until the crosslinking caused the fluid vortex to completely close and the top of the fluid to become static.

#### EXAMPLE I

Various concentrations of magnesium peroxide were evaluated as breakers for the fracturing fluid at various temperatures as indicated in Table I. Commercial magnesium peroxide comprising 25% MgO<sub>2</sub> in a mixture with MgO and Mg(OH)<sub>2</sub> was used as the source of magnesium peroxide.

The viscosity of the fracturing fluid was measured after various elapsed times at the indicated temperature, and the relative % polysaccharide breakdown was calculated using the formula:

$$\% \text{ Polysaccharide Breakdown} = \frac{(\text{Initial Viscosity} - \text{Measured Viscosity})}{\text{Initial Viscosity}} \times 100$$

The data obtained are given in Table I.

Table I

MgO <sub>2</sub> <sup>(1)</sup>		% Polysaccharide Breakdown After The									
Concentration	Temp.	Indicated Elapsed Time, Minutes									
kg/m <sup>3</sup>	°F	0	30	60	90	120	150	180	240	300	
1.2	175	0	0	0	0	0	--	15	95	100	
1.2	200	0	0	10	20	60	90	100	--	--	
0.3	250	0	0	0	20	100	--	--	--	--	
1.2	250	0	25	50	75	100	--	--	--	--	

(1) 100% active basis

#### Example II

Various concentrations of calcium peroxide were evaluated as breakers for the fracturing fluid at various temperatures as indicated in Table II. Commercial calcium peroxide comprising 75% CaO<sub>2</sub> and 25% of a mixture of calcium hydroxide and calcium carbonate was used as the source of calcium peroxide. The viscosity of the treated fracturing fluid was measured after various elapsed times at the indicated temperature. The viscosity, in centipoise, was measured at 100 rpm with a Modified Fann rheometer of the type set forth in the American Petroleum Institute Standard API RP 13B. The data obtained are given in Table II.

Comparison of the data in Tables I and II indicate that calcium peroxide is more effective than magnesium peroxide in breaking down the polymer at lower temperatures. Magnesium peroxide can be added to a fluid containing a polysaccharide polymer to produce a delayed break at relatively high temperatures, whereas cal-

cium peroxide can be added to produce a delayed break at relatively low temperatures.

Table II

$\text{CaO}_2^{(1)}$		Viscosity After The Indicated Elapsed Time, Minutes									
Concentration	Temp.										
$\text{kg/m}^3$	$^{\circ}\text{F}$	30	60	90	120	150	180	210	240	1200	
0.43	100	(2)	(2)	(2)	(2)	(2)	(2)	87	--	6	
0.43	120	162	19.5	9	6	6	--	--	--	4.5	
0.07	150	(2)	352	216	174	219	165	--	--	--	
0.07	175	(2)	(2)	198	201	--	10	--	7.5	--	
0.07	200	265	7.5	6	4.5	4.5	--	--	--	--	

(1) 100% active base

(2) Too viscous to measure

#### Claims

1. A method of decreasing the viscosity of an alkaline aqueous fluid having a hydrophilic polysaccharide polymer hydrated therein which comprises adding to the fluid a peroxide selected from the group consisting of alkaline earth metal peroxides, zinc peroxide, and mixtures thereof, and increasing the temperature of the fluid to activate the peroxide.
2. The method of Claim 1 wherein the concentration of the peroxide is from about 0.01  $\text{kg/m}^3$  to about 1.8  $\text{kg/m}^3$ .
3. The method of Claim 1 wherein the peroxide is selected from the group consisting of calcium peroxide, magnesium peroxide, and mixtures thereof.
4. The method of Claim 3 wherein the concentration of the calcium peroxide when present is within the range from about 0.01  $\text{kg/m}^3$  to about 1.0  $\text{kg/m}^3$ , and wherein the concentration of the magnesium peroxide when present is within the range from about 0.18  $\text{kg/m}^3$  to about 1.8  $\text{kg/m}^3$ .
5. The method of Claim 1, 2, 3, or 4 wherein the polymer is hydroxypropyl guar.
6. The method for the delayed breaking of an alkaline fracturing fluid having a hydrophilic polysaccharide polymer hydrated therein which comprises adding to the fluid a peroxide selected from the group consisting of alkaline earth metal peroxides, zinc peroxide, and mixtures thereof and raising the temperature of the fluid after the fluid has been used to fracture a subterranean formation by allowing the fluid to remain in the fractured formation for a period of time sufficient to effect breakdown of the polymer.
7. The method of Claim 5 wherein the concentration of the peroxide is from about 0.01  $\text{kg/m}^3$  to about 1.8  $\text{kg/m}^3$ .
8. The method of Claim 5 wherein the peroxide is selected from the group consisting of calcium peroxide, magnesium peroxide, and mixtures thereof.
9. The method of Claim 7 wherein the concentration of the calcium peroxide when present is within the range

from about 0.01 kg/m<sup>3</sup> to about 1.0 kg/m<sup>3</sup>, and wherein the concentration of the magnesium peroxide when present is within the range from about 0.18 kg/m<sup>3</sup> to about 1.8 kg/m<sup>3</sup>.

10. The method of Claim 6, 7, 8, or 9 wherein the polymer is hydroxypropyl guar.

11. In an alkaline fluid comprising an aqueous liquid, a water-soluble hydrophilic polysaccharide polymer hydrated in the aqueous liquid, and a delayed breaker for significantly decreasing the viscosity of the fluid only after the fluid has performed its intended function, the improvement which comprises utilizing as the delayed breaker a peroxide selected from the group consisting of alkaline earth metal peroxides, zinc peroxide, and mixtures thereof.

12. The fluid of Claim 11 wherein the concentration of the peroxide is from about 0.01 kg/m<sup>3</sup> to about 1.8 kg/m<sup>3</sup>.

13. The fluid of Claim 11 wherein the peroxide is selected from the group consisting of calcium peroxide, magnesium peroxide, and mixtures thereof.

14. The fluid of Claim 13 wherein the concentration of the calcium peroxide when present is within the range from about 0.01 kg/m<sup>3</sup> to about 1.0 kg/m<sup>3</sup>, and wherein the concentration of the magnesium peroxide when present is from about 0.18 kg/m<sup>3</sup> to about 1.8 kg/m<sup>3</sup>.

15. The fluid of Claim 11, 12, 13, or 14 wherein the polymer is hydroxypropyl guar and the fluid is a fracturing fluid.





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number : **0 559 418 A3**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number : **93301541.4**

(51) Int. Cl.<sup>5</sup> : **E21B 43/26, E21B 37/06,  
E21B 43/25, E21B 33/138**

(22) Date of filing : **01.03.93**

(30) Priority : **02.03.92 US 844167**

(43) Date of publication of application :  
**08.09.93 Bulletin 93/36**

(84) Designated Contracting States :  
**DE FR GB NL**

(88) Date of deferred publication of search report :  
**23.02.94 Bulletin 94/08**

(71) Applicant : **TEXAS UNITED CHEMICAL  
CORPORATION  
2000 West Loop South Suite 990  
Houston, TX 77027 (US)**

(72) Inventor : **Mondshine, Thomas, C.  
6619 Burning Tree Street  
Houston, Texas 77036 (US)**

(74) Representative : **Fisher, Adrian John et al  
CARPMAELS & RANSFORD 43 Bloomsbury  
Square  
London WC1A 2RA (GB)**

(54) **Process for decomposing polysaccharides in alkaline aqueous systems.**

(57) Alkaline earth metal or transition metal peroxides are used as a delayed breaker in alkaline aqueous fluids containing a water soluble hydrophilic polysaccharide polymer hydrated therein. The peroxide is activated by increasing the temperature of the fluid. The invention is particularly useful for the delayed break of hydraulic fracturing fluids containing hydroxypropyl guar polymer.

**EP 0 559 418 A3**

Jouve, 18, rue Saint-Denis, 75001 PARIS



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 93 30 1541 4

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	US-A-3 167 510 (E.N.ALTER) * column 2, line 56 - column 3, line 5; claim 1 * ---	1-10	E21B43/26 E21B37/06 E21B43/25 E21B33/138
D,A	US-A-4 741 401 (W.E.WALLES) * claims 1,17 * ---	1,11-15	
D,A	US-A-4 369 843 (T.C.MOND SHINE) * claim 1 * ---	1	
D,A	US-A-3 259 584 (J.R.MOYER) * claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			E21B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 December 1993	Examiner Rotsaert, L
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			